Aqueous Chemistry

Shallow lake and pond environments typically exhibit highly stochastic temporal dynamics in physico-chemical parameters due to hydrodynamic considerations. Such environments are further characterized by such qualities of low total nitrogen (TN) to total phosphorus (TP) ratios, low stratification, high primary productivity, and substantial internal transport of sediments by resuspension and sedimentation.

FIGURE 3.1 Lake Tuendae, a shallow, artificially-constructed aquatic habitat located in the Soda Basin of the Mojave Desert, California, USA. Two distinct aquifer systems influence this region: a carbonate rock-based system and the Mojave River Sink recharged from percolation.

Harsh desert conditions such as those observed in Lake Tuendae, Mojave Desert, USA, add to the complication of assessing and managing the health of aquatic species in such habitats. High evaporative desert processes are believed to play a major role in water quality dynamics. The Mojave Desert itself can undergo air temperature extremes (−6.7° to 40.6°C). Moreover, Lake Tuendae has limited protection from evaporation and is reported to sustain an annual evaporative loss of nearly 410,000 ft³. Scientists are thus actively involved in studying this region for greater understanding of the physico-chemical makeup of shallow desert aquatic environments.
3.1. CHEMICAL COMPOSITION AND PROPERTIES OF WATER

Water has many unique properties and characteristics that contribute to its role as being nature’s miracle worker. Given the complex nature of the water cycle and its role in many chemical, biological, and physical processes, and given the fact that such processes are crudely evaluated in lower division courses, reinforcement of the basic properties of water is warranted.

3.1.1. Atomic Structure and Hydrogen Bonding

Water’s atomic structure is simple (Figure 3.2a), consisting of two hydrogen atoms bonded to one oxygen atom. The nature of the structure of water causes its molecules to possess unique molecular polarity with a partial negative charge ($\delta^-$) near the oxygen atom due to the unshared pairs of electrons and partial positive charges ($\delta^+$) near the hydrogen atoms. Electrostatic attractions between the partial positive charge near the hydrogen atoms and the partial negative charge near the oxygen results in the formation of hydrogen bonds as shown in Figure 3.2b. Water’s polar nature is due to the unequal sharing of its electrons in a bent structure. This molecular polarity causes water to be a powerful solvent giving rise to various types of reactions in aqueous solutions—a main focus of this chapter. The hydrophobic effect (the exclusion of compounds containing carbon and hydrogen

![Figure 3.2](image)

**FIGURE 3.2** a) An electrically neutral water molecule. Note the partial negative charge, denoted as $\delta^-$ (the O atom), and the partial positive charge, denoted as $\delta^+$ (the H atom). b) Hydrogen bonding between water molecules.
(non-polar compounds)) is another unique property of water caused by the hydrogen bonds. Other unique properties of water are described below.

Water is also the only substance on Earth that exists in all three physical states of matter: liquid, solid, and gas (Figure 3.3). In a liquid state, water molecules are constantly moving in relation to each other, and the hydrogen bonds are continually breaking and reforming at unprecedented timescales. In solid form (ice), motion is minimized and molecules become oriented to form a strong, open-lattice structure. When comparing the structure of ice and water in a liquid state, empty spaces within the ice structure result, allowing a more open structure. This structure takes up more volume than liquid water and hence ice is less dense. What unique role then does water’s existence in different physical states have on the environment? Consider that massive amounts of heat exchange are incorporated in such changes of state. And as we learned in Chapter 1, oceans and other large water bodies have a noticeable influence on climate. They do this by acting as heat reservoirs and heat exchangers and the source of the majority of rain and snow that falls over land masses.

**FIGURE 3.3** Phase diagram of water showing its preferred states at different temperatures and pressure. At typical temperatures and pressures on Earth, water is a liquid, but becomes solid if its temperature is lowered below 273 K and gaseous if its temperature is raised above 373 K, at the same pressure. A triple point is where three phase lines join. Here, three phases stably coexist but may abruptly change into each other, given a slight change in temperature or pressure. A critical point occurs at the end of a phase line where the properties of the two phases become indistinguishable from each other.
3.1.2. Surface Tension and Heat Capacity

The hydrogen bonding exhibited by water molecules allows for the properties of strong surface tension and high heat capacity. **Surface tension** is the tendency of molecules of liquid to “stick” together at the surface. Water has strong surface tension due to its polarity and hydrogen bonding. In nature, water has one of the highest surface tensions, 72.8 mN/m (at 20°C), exceeded by only a few liquids including mercury (surface tension of about 480 mN/m). Surface tension plays an important role in air/water interface interactions. Surface tension also plays a role in energy transfer from wind to water, resulting in wave formation. Waves play important roles in helping oxygen diffuse in lakes and oceans (Figure 3.4).

**Heat capacity** is defined as the amount of heat required to raise the temperature of a mass of substance by 1°C. The heat capacity for one gram of substance is called its **specific heat**, \( C_s \), given by

\[
C_s = \frac{q}{m \Delta T},
\]  

(3.1)

where \( m \) = mass of substance, \( \Delta T \) = the change in temperature, and \( q \) = the loss or gain of a specific quantity of heat. Note that specific heat can vary with temperature; hence for more precise measurements the temperature is specified. The specific heat of water (liquid) is 4.184 Joules/g°C, one of the highest specific heats of all substances. Upon rearrangement, Equation 3.1 becomes

\[
q = C_s m \Delta T.
\]  

(3.2)

Here, one can calculate the quantity of heat gained or lost by using its specific heat together with its mass and change in temperature. The ability of water to stabilize temperature depends on its relatively high specific heat, thus playing

**FIGURE 3.4** Wind-generated surface waves are controlled by the velocity of the wind, wind duration, and fetch. Surface tension is the direct result of the wind stress exerted on the sea surface. Most wind-generated waves eventually reach shorelines and dissipate.
an important role in the Earth’s climate through its cooling and transfer of heat effects in thermal and chemical processes. But in the world’s oceans, heat capacities are affected by temperature, salinity, and pressure. For example, at a salinity of 35 parts per thousand (ppth), a temperature of 25°C, and under constant pressure conditions, the heat capacity of seawater is 3.995 Joules/g°C. Thus, 3,995 joules of energy are required to heat 1.0 kilogram of seawater by 1.0°C.

### 3.1.3. Water Density

The physical properties temperature, pressure, and salinity work together to determine water density (weight of water divided by the amount of space it occupies). The high density characteristic of liquid water is largely due to the cohesive nature of the hydrogen-bonded network discussed earlier. This reduces the free volume and ensures a relatively high density, partially compensating for the open nature of the hydrogen-bonding effect. Water’s density changes with respect to temperature, but not on a linear scale as shown in Figure 3.5. Maximum density (at 3.984°C) is the result of the opposing effects of increasing temperature, causing both structural collapse that increases density and thermal expansion that lowers density. Increasing pressure shifts

![Figure 3.5](image-url)  
**Figure 3.5** A graph illustrating a display of the relationship between temperature and density of water at normal atmospheric pressure.
the water equilibrium toward a more collapsed structure. Although pressure will increase the density of water at all temperatures (thus flattening the temperature density curve), there will be a disproportionate effect at lower temperatures.

**Example Problem 3.1**

As discussed, pressure will increase the density of water at all temperatures, with a disproportionate effect at lower temperatures. What would be the result of this occurrence? What is the effect at elevated pressures?

**Answer:** The result is a shift in the temperature of maximum density to lower temperatures. At high enough pressures the density maximum is shifted to below 0°C.

Density maximum ensures that the bottoms of freezing freshwater lakes generally remain at about 4°C and thus unfrozen. The change in density with temperature causes an inversion in cold water systems as the temperature is raised above about 4°C. Thus, in water below about 4°C, warmer water sinks whereas when above about 4°C, warmer water rises. As water warms up or cools down through 4°C, such **thermal stratification** causes considerable mixing with useful consequences such as increased gas exchange. During summer stratification in colder climates, for example, moderately deep lake waters stratify into fairly distinct layers: the **epilimnion**, **metalimnion**, and **hypolimnion**. The epilimnion is the warmer, upper layer influenced by surface wind mixing and readily exchanges dissolved gases with the atmosphere. The metalimnion is the transitional layer where temperatures rapidly change. It houses the **thermocline**, the horizontal plane where the greatest water temperature changes occur. Below the metalimnion and extending to the bottom of the lake is the colder, and relatively undisturbed, hypolimnion.

Water density is also affected by salinity (with temperature having a greater overall effect) as shown in Figure 3.6. Salinity is an indicator of the total amount of dissolved salts in water, typically expressed in ppth. Freshwater salinity is usually less than 0.5 ppth. Water between 0.5 ppth and 17 ppth is called brackish, such as those found in the world’s estuaries. The average ocean salinity is 35 ppth. This number varies between about 32 and 37 ppth due to melting of ice, inflow of river water, evaporation, rain, snowfall, wind, wave motion, and ocean currents that cause horizontal and vertical mixing of the saltwater.

A few points must be made in regards to density and the world’s oceans. The circulation of surface waters of the ocean is driven by winds, whereas the circulation of the deep waters is driven by differences in density. **Thermohaline circulation** refers to the process of circulation in the ocean depths. Water has a tendency to move horizontally throughout the deep ocean, moving along lines of equal density. One would thus expect that vertical
circulation is limited due to the ease of water to move along lines of constant density (isopycnals) than across them.

### 3.2. ACID-BASE PHENOMENA

In pure water, the majority of the water molecules remain intact. However, a small amount will collide with one another to cause the self-ionization reaction represented by

\[
\text{H}_2\text{O} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^- \quad K_w = 1.0 \times 10^{-14} \quad \text{at 25°C.} \quad (3.3)
\]

Here, [H$_3$O$^+$] and [OH$^-$] are 1.0 x 10$^{-7}$ M. It is the 7 in the exponent of this number that gives neutral water a pH of 7.00 since [H$_3$O$^+$]=[OH$^-$]. For pH, we express the activity of the hydronium ion by means of its negative logarithm:

\[
\text{pH} = -\log_{10}[\text{H}_3\text{O}^+]. \quad (3.4)
\]

$K_w$ is sensitive to both pressure and temperature; it increases when either increases. Similarly, to express the [OH$^-$], the pOH scale can be used, where

\[
\text{pOH} = -\log_{10}[\text{OH}^-]. \quad (3.5)
\]
Measurements of pH are typically expressed to two decimal places, given that, on the whole, practical problems restrict the accuracy of most pH measurements to two places. Ostensibly, the two decimal places imply that there are only two significant figures in the $\text{H}_3\text{O}^+$ concentration.

**TEXTBOX 3.1**

The term *hydronium ion* ($\text{H}_3\text{O}^+$) is often substituted for *hydrogen ion* to reflect the association of a hydrogen ion with a molecule of water. Note: $\text{H}^+$ and $\text{H}_3\text{O}^+$ are used interchangeably to describe the same species in water solutions.

**Example Problem 3.2**

Derive a relationship between pH and pOH so that the sum of the pH and pOH = 14.00 (at 25°C).

**Answer:** The relationship between pH and pOH is dictated by the expression that describes the ionization of water:

$$[\text{H}_3\text{O}^+] [\text{OH}^-] = K_w.$$  

An expression can be derived for pH and pOH by taking the negative logarithm of both sides:

$$-\log[\text{H}_3\text{O}^+] [\text{OH}^-] = -\log(K_w).$$

The logarithm of a product can be written as the sum of the two logarithms, therefore:

$$-\log[\text{H}_3\text{O}^+] - \log[\text{OH}^-] = -\log(K_w).$$

Realizing that the p-function $= -\log$, we can rewrite

$$\text{pH} + \text{pOH} = \text{p}K_w.$$  

Since the numerical value for $\text{p}K_w = 14$, the relationship can be written as

$$\text{pH} + \text{pOH} = 14.00.$$  

For any acid-base system, a **mass balance** equation can be written that relates the concentrations of the various dissociation products of the substance to its **formal concentration** $C_F$. The mass balance equation expresses the conservation of mass in the form of atoms and groups of atoms that get distributed in a mixture or solution. Viewed another way, it states that the number of moles of an element placed in a solution will equal the total number of moles of that element in all the chemical forms it may adopt while in the solution. Let’s consider a basic HCl solution with its mass balance expression shown as follows:

$$[\text{HCl}] + [\text{Cl}^-] = C_F.$$  

But since HCl is a strong acid, we can neglect the first term and write the trivial mass balance equation:

$$[\text{Cl}^-] = C_F.$$  

(3.6)
Note that the dissociation equilibrium of water must always be satisfied, where

$$[\text{H}_3\text{O}^+][\text{OH}^-] = K_w.$$  \hspace{1cm} (3.7)

In any ionic solution, the sum of the positive and negative electric charges must be zero; in other words, all solutions are electrically neutral. This **charge balance** is expressed in terms of the concentration of positive and negative charges, taking into account not only the molar concentration of the cations and anions but of their individual charges as well.

$$[\text{H}_3\text{O}^+] = [\text{OH}^-] + [\text{Cl}^-]$$ \hspace{1cm} (3.8)

In our approach, we must combine the above concepts into a single expression that relates $[\text{H}_3\text{O}^+]$ to $C_F$. By substituting Equation 3.6 into Equation 3.7, we can get rid of $[\text{Cl}^-]$:

$$[\text{H}_3\text{O}^+] = [\text{OH}^-] + C_F.$$ \hspace{1cm} (3.9)

Using Equation 3.7 allows the $[\text{OH}^-]$ term to be eliminated:

$$[\text{H}_3\text{O}^+] = C_F + \frac{K_w}{[\text{H}_3\text{O}^+]}.$$ \hspace{1cm} (3.10)

It should be obvious from Equation 3.10 that the $[\text{H}_3\text{O}^+]$ will be the same as the formal concentration as long as the solution is not very dilute.

For proper discussion of natural waters, we must consider the importance of a variety of weak acids, weak bases, and mineral assemblages characteristically present. Natural water composition is controlled by a combination of geochemical and biological processes and is largely affected by such parameters as pH and alkalinity. Alkalinity or Total Alkalinity ($A_T$) is a measure of the carbonate ($\text{CO}_3^{2-}$), bicarbonate ($\text{HCO}_3^-$), and hydroxide ($\text{OH}^-$) ions present in aqueous systems. Of additional consideration are borates, silicates, phosphates, ammonium, sulfides, and organic ligands. Ostensibly, alkalinity is a measure of the buffering capacity of water or the capacity of bases to neutralize acids. In the natural environment $\text{CO}_3^{2-}$ alkalinity comprises the majority of the $A_T$ due to the common occurrence and dissolution of carbonate rocks and the presence of $\text{CO}_2$ in the atmosphere. Such concepts will be discussed extensively in section 3.2.1.

Measuring alkalinity is important, for example, in determining a water system’s ability to neutralize acidic pollution from rainfall or wastewater processes. Alkalinity of surface and groundwater is directly related to the underlying sediment and bedrock. Areas underlain by rocks and sediment rich in calcium from limestone, for example, are more resistant to changes in pH. Alkalinity also helps regulate the metal content of natural waters. For example, $\text{CO}_3^{2-}$ and $\text{HCO}_3^-$ in aqueous systems can remove toxic metals (e.g., lead, arsenic, barium, and cadmium) by precipitating the metals out
of solution. For instance, barium forms an insoluble salt when reacting with \( \text{CO}_3^{2-} \):

\[
\text{Ba}^{2+} + \text{CO}_3^{2-} \rightleftharpoons \text{BaCO}_3(s).
\]

Barium is a common metal found in industrial wastewater streams and can be effectively removed to acceptable levels by precipitating the metal in the insoluble form above.

### 3.2.1. The Carbonate System in Aquatic Systems

Discussion in Chapter 1 touched upon \( \text{CO}_2 \) being the dominant end product of organic carbon degradation in most aquatic environments, with its variation being a measure of net ecosystem metabolism. Let’s consider such a topic in greater detail. This section deals with the functioning carbonate system in aquatic environments in concurrence with atmospheric \( \text{CO}_2 \) and sedimental \( \text{CaCO}_3 \). We will learn how the carbonate system dominates pH control in most aquatic systems and thus regulates numerous global biogeochemical processes. Major discussion will be centered on the distribution of carbonate species in aqueous solutions with detailed reference to the carbonate system and its buffering source in the world’s oceans.

Carbon dioxide is exchanged between the atmosphere and aquatic systems via equilibrium of \( \text{CO}_2(g) \) and dissolved \( \text{CO}_2 \). Central to further discussion are four measurable parameters: \( \text{pH} \), \( p\text{CO}_2 \), \( A_T \), and total dissolved inorganic carbon (DIC). Dissolved \( \text{CO}_2 \) reacts with aqueous systems, ultimately becoming part of the carbonate system through various forms:

\[
\text{CO}_2(aq) + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3 \rightleftharpoons \text{HCO}_3^- + \text{H}^+ \rightleftharpoons \text{CO}_3^{2-} + 2\text{H}^+.
\] (3.11)

Dissolved \( \text{CO}_2 \) in oceans occurs mainly in three inorganic forms: free aqueous carbon dioxide (\( \text{CO}_2(aq) \)), bicarbonate (\( \text{HCO}_3^- \)), and carbonate ion (\( \text{CO}_3^{2-} \)). A minor form is true carbonic acid (\( \text{H}_2\text{CO}_3 \)) whose concentration is less than 0.3% of \([\text{CO}_2(aq)]\). Note that the sum of \([\text{CO}_2(aq)]\) and \([\text{H}_2\text{CO}_3]\) is denoted as \([\text{CO}_2]\). In thermodynamic equilibrium, gaseous carbon dioxide (\( \text{CO}_2(g) \)) and \([\text{CO}_2]\) are related by Henry’s law:

\[
\text{CO}_2(g) \rightleftharpoons \text{CO}_2, K_0[\text{CO}_2],
\]

where \( K_0 \) is the temperature and salinity-dependent solubility coefficient of \( \text{CO}_2 \) in seawater (Weiss, 1974).

The majority of dissolved inorganic carbon (DIC) in the world’s oceans is in the form of \( \text{HCO}_3^- \) (>85%), with DIC described further in Textbox 3.2. Once dissolved, a small portion of the \( \text{CO}_2 \) reacts with water to form \( \text{H}_2\text{CO}_3 \):

\[
\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3
\] (3.12)
Overall, the following equilibria are established in any carbonate-containing solution:

\[
\frac{[H^+][HCO_3^-]}{[H_2CO_3]} = K_1 = 10^{-6.3}
\]

\[
\frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} = K_2 = 10^{-10.3}
\]

Considering the relationship \([H_3O^+][OH^-] = K_w\),

\[
C_T = [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}] \quad \text{(mass balance)}
\]

\[
[H^+] = [HCO_3^-] - 2[CO_3^{2-}] - [OH^-] = 0 \quad \text{(charge balance)}.
\]

Note that \(C_T\) = the sum of all carbonate species concentrations.

**TEXTBOX 3.2**

The **partial pressure of carbon dioxide** (\(pCO_2\)) is the gas phase pressure of CO₂, which would be in equilibrium with the dissolved CO₂. \(pCO_2\) measurements provide a relative measure of trophic status in the water column as a result of the balance between the capacity of an aqueous system to decompose organic matter and its capacity to take up CO₂ through photosynthesis. \(pCO_2\) can be calculated from any two of the following parameters (together with temperature and salinity): pH, \(A_T\), and DIC, are measured directly by equilibrating air (or another carrier gas) with water and then measuring the \(pCO_2\) of the equilibrated air by either gas chromatography or infrared spectroscopy.

**Dissolved inorganic carbon** (DIC) is defined as

\[
\text{DIC} = [CO_2] + [HCO_3^-] + [CO_3^{2-}].
\]

DIC is an important parameter when performing measurements related to the pH of natural aqueous systems and CO₂ flux estimates. DIC is measured by the acidification of the sample, which drives the equilibria to CO₂. This gas is then **sparged** from solution and trapped, with the extracted quantity subsequently measured, typically by a coulometer or by an infrared CO₂ analyzer.

Like all acids, \(H_2CO_3\) releases \(H^+\) into the solution, leaving both \(HCO_3^-\) and \(CO_3^{2-}\) in the solution. The acidity of ocean waters is in turn determined by \([H^+]\), which is measured on the pH scale. What effect does this have on the world’s oceans and biological processes? It has been estimated that over the last 200 years, oceans have taken up an excess of inorganic carbon from the atmosphere equivalent to approximately 25—30% of the total emissions of CO₂ from fossil-fuel burning, cement manufacturing, and land use change since the beginning of the industrial revolution (Sabine, et al., 2004). While this uptake potentially slows the growth rate in atmospheric CO₂, it is reported to lower
surface water pH, with the potential for the resulting ocean acidification to disrupt marine ecosystems. For example, ocean acidification may limit corals and other coralline plants and animals to properly synthesize their carbonate skeletal materials (via the formation of biogenic calcium carbonate, CaCO$_3$) due to their ability to calcify being pH dependent. Even in today’s saturated CaCO$_3$ oceans, calcification rates and [CO$_3^{2-}$] continue to decline. As anthropogenic carbon emissions continue to accelerate, the CO$_2$ contained in these emissions will likely continue to reduce the alkalinity of the oceans.

### 3.2.2. Carbonate Species Distribution

In order to gain a true understanding of the distribution of carbonate species in aqueous systems we must consider pH in greater detail. To do this, determination of whether aqueous systems are in equilibrium with the atmosphere is paramount. Recall our Chapter 1 discussion of open and closed systems, which will aid in this determination. If aqueous systems are in equilibrium with the atmosphere, $p$CO$_2$ remains constant and the concentration of [CO$_2$] is fixed. This is considered an open system as is the case for streams, shallow lake environments, and upper regions of the world’s oceans where wind mixing is prevalent. However, even though the concentration of [CO$_2$] is fixed, it does not mean that the total carbonate concentration is fixed since variable amounts of dissociated forms of carbonate, i.e., HCO$_3^-$ and CO$_3^{2-}$, will be present depending on the pH. If we know the pH and the $p$CO$_2$ for an open system, we can calculate the concentrations of all relevant species in the system from the mass-action expressions, which include the Henry’s law constraint ($K_{CO_2}$), the dissociation constants of carbonic acid ($K_1$, $K_2$), and $K_w$.

A Bjerrum plot can be constructed to show the concentrations of various inorganic carbon species as a function of pH in both an open and closed CO$_2$-H$_2$O system format. Such plots are typically used by marine chemists to track the response of an ocean to changes both in pH and of inputs in carbonate and CO$_2$. Consider Figure 3.7, which provides a plot of log concentration (molar) vs. pH for an open CO$_2$-H$_2$O system at 25°C with $p$CO$_2 = 10^{-3.5}$ atm. Upon inspection, this plot shows the pH ranges in which the three different carbonate species are predominant. At pH $< pK_1$, [CO$_2$] is the predominant species. At this pH range it accounts for nearly all of the total carbonate, and in theory, a line for total carbonate could be drawn to coincide with the line showing [CO$_2$]. Notice that [CO$_2$] is independent of pH (and so is the total carbonate concentration at this point). At pH $= pK_1$, [CO$_2$] and HCO$_3^-$ are at equal concentrations, which results in the total carbonate concentration being double the concentration of either of these species. This would result in the total carbonate curve rising 0.301 log units above the point at pH $= pK_1$. Here, carbonate ion contributes negligibly to total carbonate at this pH. At $pK_1 < pH < pK_2$, HCO$_3^-$ is the predominant species, with its concentration approximately equal to total carbonate. Finally, at pH $> pK_2$, CO$_3^{2-}$ will be
the predominant species. A theoretical total carbonate curve would thus follow $\text{CO}_2^2-$. A Bjerrum plot of various inorganic carbon species as a function of pH in a closed system for a value of total inorganic carbon of $10^{-3}$ mol L$^{-1}$ is shown in Figure 3.8. Let’s examine this plot as we did for the open CO$_2$-H$_2$O system. Notice that at pH $< pK_1$, [CO$_2$] is dominating and accounts for nearly all of the
total carbonate. Here, \([\text{CO}_2]\) plots as a horizontal line. If we consider \(pK_1 < pH < pK_2\), \(\text{HCO}_3^-\) is predominant and accounting for nearly all of the total carbonate present. In this pH range, \([\text{CO}_2]\) begins to descend away towards higher pH. Upon approaching \(pK_2\), \(\text{HCO}_3^-\) begins to drop. Finally, at \(pH > pK_2\), \([\text{CO}_2]\) continues its descent toward a higher pH, \(\text{CO}_3^{2-}\) is predominant, and its concentration plots as a horizontal line. In addition, the \(\text{HCO}_3^-\) line descends toward a higher pH. Examples of closed \(\text{CO}_2-\text{H}_2\text{O}\) systems include waterbodies with deep regions of stratification and the air component of soils.

### 3.3. OXIDATION-REDUCTION IN NATURAL WATERS

Numerous oxidation-reduction (redox) reactions take place in natural waters, which have strong influences on the behavior (e.g., solubility, mobility, and bioavailability) of elements in such systems. Analogous to acid-base reactions discussed earlier, which involve the transfer of a proton (\(\text{H}^+\)), redox reactions involve the transfer of an electron (\(e^-\)). However, unlike free hydrated protons, free hydrated electrons do not exist. Therefore, every reduction reaction must be accompanied by a corresponding oxidation reaction. A redox reaction can be considered a pair of coupled half-reactions—a half-reaction of oxidation and a half-reaction of reduction. Consider the following two half-reactions:

\[
\begin{align*}
\text{Zn(s)} & \rightarrow \text{Zn}^{2+}(\text{aq}) + 2e^- \\
\text{Cu}^{2+}(\text{aq}) + 2e^- & \rightarrow \text{Cu(s)}.
\end{align*}
\]

Here, \(\text{Zn(s)}\) is oxidized and causes reduction of \(\text{Cu}^{2+}(\text{aq})\). It is therefore the reducing agent. \(\text{Cu}^{2+}(\text{aq})\) is reduced and causes oxidation of \(\text{Zn(s)}\), thus it is the oxidizing agent. The overall reaction is achieved by adding the two half-reactions so that the electrons in the two half-reactions cancel:

\[
\text{Cu}^{2+}(\text{aq}) + \text{Zn(s)} \rightarrow \text{Cu(s)} + \text{Zn}^{2+}(\text{aq}).
\]

Note: In acidic or basic solutions, one may need to add \(\text{H}^+, \text{OH}^-\), or \(\text{H}_2\text{O}\) to balance both equations.

As you study the redox reactions below, keep in mind that redox equilibrium is not well established due to the presence of living organisms, the dependence of most redox reactions on biological catalysis, and the slow kinetics of many oxidation and reduction reactions. One should be cautious when interpreting redox information, since reactions are very slow in the natural environment. In addition, some redox species may not be electroactive in environmental systems. Potential limitations to redox potential measurements in natural waters will also be discussed.

As an example half-reaction of environmental significance, organic pollutants (e.g., non-biodegradable organic matter in pigment wastewater) and other wastes (e.g., pesticides) can be mineralized upon oxidation by powerful oxidizing agents like hydrogen peroxide (\(\text{H}_2\text{O}_2\)), which through the following reaction...
Fe\(^{2+}\) + H\(_2\)O\(_2\) → Fe\(^{3+}\) + OH\(^-\) + •OH

produces an oxidizer intermediate: the hydroxyl radical (•OH). The efficiency of this process depends on H\(_2\)O\(_2\) and Fe\(^{2+}\) concentrations and pH (optimal range: pH 3.0–5.0) of the reaction. The initial concentrations of the pollutant and temperature also have a substantial influence on the final efficiency.

U.S. Air Force scientists have recently acknowledged the role of hydrogen as a direct electron donor in the anaerobic dechlorination of chlorinated aliphatic hydrocarbons (CAHs). Consider the reduction of perchloroethene (PCE) in groundwater. Initially, molecular hydrogen disassociates in the following half-cell reaction:

\[
\text{H}_2 \rightarrow 2\text{H}^+ + 2e^- \quad (3.17)
\]

Next, PCE is reduced by the substitution of a chloride ion with a hydrogen ion and the transfer of one electron:

\[
\text{C}_2\text{Cl}_4 + 2\text{H}^+ + 2e^- \rightarrow \text{C}_2\text{HCl}_3 + \text{H}^+ + \text{Cl}^- \quad (3.18)
\]

The hydrogen ion and chloride ion produced likely form HCl as follows:

\[
\text{H}^+ + \text{Cl}^- \rightarrow \text{HCl} \quad (3.19)
\]

Combining and balancing Equations 3.17, 3.18, and 3.19, the dechlorination of PCE using hydrogen as the electron donor can be written as follows:

\[
\text{H}_2 + \text{C}_2\text{Cl}_4 \rightarrow \text{C}_2\text{HCl}_3 + \text{HCl} \quad (3.20)
\]

Anaerobic reductive dechlorination is performed by limited metabolic classifications of bacteria. These groups may act differently from one another, and include methanogens, sulfate-reducing bacteria, and dechlorinating bacteria.

### 3.3.1. Redox Variables

Many variables are commonly employed to express redox conditions: Eh, p\(\varepsilon\), \(f_{\text{O}_2}\) (fugacity of oxygen), and \(f_{\text{H}_2}\) (fugacity of hydrogen). They are all more or less useful depending on a specific problem, or an approach to measurements or calculations, and can be readily converted from one to the other given the appropriate conversion factors. Fugacity of hydrogen, \(f_{\text{H}_2}\), is a convenient parameter because any redox reaction can be written to include hydrogen as a product or reactant. High values of \(\log f_{\text{H}_2}\) indicate reducing conditions whereas low \(\log f_{\text{H}_2}\) values indicate oxidizing conditions. Some of the most important redox reactions in natural waters are the oxidation of organic matter and the corresponding reduction reactions: reduction of oxygen to H\(_2\)O, nitrate to elementary nitrogen N\(_2\), manganese(III/IV) to Mn(II), Fe(III) to Fe(II), sulfate to sulfide, and CO\(_2\) to methane. A few specific examples are provided below. Diagrams that show the dominant ionic or solid phase forms of redox
reaction participants as a function of pH and Eh (or of pH and p_\text{e} or f_{H_2}) are useful ways of summarizing equilibrium speciation for a variety of conditions.

**TEXTBOX 3.3**

**Eh** is the redox potential of a solution and a measure of the relative intensity of oxidizing or reducing conditions in a given system. It is expressed in volts and at equilibrium can be expressed by standard equations of chemical thermodynamics. **Electron activity**, p_e, indicates the tendency of a solution to donate or accept a proton. If p_e is low, the solution is reducing. Alternatively, if p_e is high, the solution is oxidizing. **Fugacity** is a calculated property that is intrinsically related to chemical potential. Fugacity is a measure of how much the chemical potential of the component in the gas deviates from the chemical potential of some reference, namely, the standard state, due to changes in pressure and/or the mole fraction of the component.

### 3.3.2. Aqueous Nitrogen Species

Consider the representative N-O-H system at 25°C and 1 atm depicted in Figure 3.9. Shown is a f_{H_2} – pH plot that indicates both oxidation-reduction and acid-base conditions. The horizontal blue lines in the plot correspond to reducing (upper) and oxidizing (lower) boundaries in terms of log f_{H_2}, where H_2O is stable. The dissociation reaction of water is

\[
\text{H}_2\text{O} \rightleftharpoons \frac{1}{2}\text{O}_2(g) + \text{H}_2(g),
\]

where, at equilibrium,

\[
\log K = \log f_{H_2} + \frac{1}{2}\log f_{O_2}
\]

and

\[
\log f_{H_2} = \log K - \frac{1}{2}\log f_{O_2}.
\]

The usual atmospheric O_2 defines the oxidizing boundary of water stability, and we may use 0.21 atm (or log f_{O_2} = −0.68) since oxygen makes up about 21% of the atmosphere by volume. Combining with the equilibrium constant of reaction 14 in Table 3.1, this corresponds to log f_{H_2} = −41.21. The reducing boundary occurs at 1 atm H_2(g) since the pressure of hydrogen gas in surface environments cannot exceed the atmospheric pressure. This sets the upper boundary at log f_{H_2} = 0.

For the vertical line separating NH_4^+ and NH_3(aq),

\[
\text{NH}_4^+ \rightleftharpoons \text{NH}_3(aq) + \text{H}^+
\]

\[
\log K = -\text{pH} + \log a_{\text{NH}_3} - \log a_{\text{NH}_4^+}.
\]

(3.23)
If we consider $a_{\text{NH}_3} = a_{\text{NH}_4^+}$, the equation reduces to $\text{pH} = \log K$, or $\text{pH} = 9.24$. So this line corresponds to the pH where the activity of $\text{NH}_4^+$ equals the activity of $\text{NH}_3(\text{aq})$. At pH $> 9.24$, the ratio $a_{\text{NH}_4^+}/a_{\text{NH}_3}$ is greater than 1; at any pH values left of this line, less than 1.

Next, consider the redox couple between nitrite and ammonium ion:

$$\text{NO}_2^- + 2\text{H}^+ + 3\text{H}_2(\text{g}) \rightleftharpoons \text{NH}_4^+ + 2\text{H}_2\text{O}.$$ 

The equilibrium constant expression gives

$$\log K = \log a_{\text{NH}_4^+} - \log a_{\text{NO}_2^-} + 2\text{pH} - 3\log f_{\text{H}_2}.$$ 

(3.24)

Setting the activity of $\text{NH}_4^+$ equal to the activity of $\text{NO}_2^-$, rearrangement gives $\log f_{\text{H}_2}$ as a function of pH:

$$\log f_{\text{H}_2} = \frac{2}{3}\text{pH} - \frac{1}{3}\log K.$$ 

(3.25)

This equation has a slope of 2/3 and its intercept can be evaluated from the log $K$ of reaction 6 in Table 3.1, and it is plotted in Figure 3.9 as a line that separates the predominance areas for $\text{NH}_4^+$ and $\text{NO}_2^-$. Using these methods, similar lines can be constructed for the other aqueous nitrogen species. The appropriate reactions and their equilibrium constants are listed in Table 3.1. Also overlaid on the figure are dashed lines, derived from reactions 10–13, that illustrate the area of nitrogen, $\text{N}_2(\text{aq})$, dissolved in aqueous solutions in contact with the atmosphere having 78% $\text{N}_2$. 

FIGURE 3.9 A representative N-O-H system at 25°C and 1 atm. Shown is a $f_{\text{H}_2}$-pH plot that indicates both oxidation-reduction and acid-base conditions.
3.3.3. Reduced Phosphorus Species Reconsidered

While other biologically relevant elements have well-defined redox mechanisms (e.g., denitrification for the conversion of nitrate to nitrogen gas), thus far, it has been assumed that phosphorus species do not undergo redox reactions in the environment and exist solely in the phosphate, organic phosphorus esters (P-O-C bonds), and colloidal complex forms in aqueous systems. But recall our discussion in section 1.5.4 describing recent developments in the field of microbiology and research on the origin of life suggesting a possibly significant role for reduced, inorganic forms of phosphorus in bacterial metabolism and as evolutionary precursors of biological phosphate compounds.

Figure 3.10 depicts the calculated equilibrium distributions of the various species of phosphate, hypophosphite, and phosphite as a function of pH. At the circumneutral pH of most natural waters and soils, the dominant P species according to equilibrium calculations are H₂PO₄⁻ and HPO₄²⁻ for phosphate, H₂PO₃⁻ and HPO₃²⁻ for phosphite, and H₂PO₂⁻ for hypophosphite. This

<table>
<thead>
<tr>
<th>Reaction</th>
<th>log K a</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 HNO₃(aq) ⇌ NO₃⁻ + H⁺</td>
<td>1.303</td>
</tr>
<tr>
<td>2 NH₄⁺ ⇌ NH₃(aq) + H⁺</td>
<td>−9.241</td>
</tr>
<tr>
<td>3 NO₃⁻ + H⁺ + H₂(g) ⇌ HNO₂(aq) + H₂O</td>
<td>30.992</td>
</tr>
<tr>
<td>4 NO₃⁻ + H₂(g) ⇌ NO₂⁻ + H₂O</td>
<td>27.767</td>
</tr>
<tr>
<td>5 HNO₂(aq) + H⁺ + 3 H₂(g) ⇌ NH₄⁺ + 2 H₂O</td>
<td>88.155</td>
</tr>
<tr>
<td>6 NO₂⁻ + 2 H⁺ + 3 H₂(g) ⇌ NH₄⁺ + 2 H₂O</td>
<td>91.381</td>
</tr>
<tr>
<td>7 NO₂⁻ + H⁺ + 3 H₂(g) ⇌ NH₃(aq) + 2 H₂O</td>
<td>82.140</td>
</tr>
<tr>
<td>8 HNO₃(aq) + H₂(g) ⇌ HNO₂(aq) + H₂O</td>
<td>32.295</td>
</tr>
<tr>
<td>9 NO₃⁻ + 2 H⁺ + 4 H₂(g) ⇌ NH₄⁺ + 3 H₂O</td>
<td>119.147</td>
</tr>
<tr>
<td>10 NO₃⁻ + H⁺ + 5 H₂(g) + 1/2 N₂(g) ⇌ N₂(aq) + 3 H₂O</td>
<td>102.041</td>
</tr>
<tr>
<td>11 N₂(aq) + H⁺ + 3 H₂(g) ⇌ NH₄⁺ + 1/2 N₂(g)</td>
<td>7.865</td>
</tr>
<tr>
<td>12 HNO₃(aq) + 5/2 H₂(g) + 1/2 N₂(g) ⇌ N₂(aq) + 3 H₂O</td>
<td>103.344</td>
</tr>
<tr>
<td>13 N₂(aq) + 3 H₂(g) ⇌ NH₃(aq) + 1/2 N₂(g)</td>
<td>−41.552</td>
</tr>
</tbody>
</table>

aAll values of log K were calculated with ΔG°.
FIGURE 3.10  Species abundance, as a percentage of the total concentration, is shown for a) phosphate, b) phosphite, and c) hypophosphite species. At circumneutral pH (typical of surface waters), the dominant species are $H_2PO_4^-$ and $HPO_4^{2-}$ for phosphate, $H_3PO_3$ and $HPO_3^{2-}$ for phosphite, and $H_2PO_2$ for hypophosphite.
speciation is based on the following pKa values: for phosphate, pKa1 = 2.1, pKa2 = 7.2, and pKa3 = 12.7; for phosphite pKa1 = 1.3 and pKa2 = 6.7; and for hypophosphite pKa1 = 1.1. The charge of each species will determine the environmentally relevant reactions (such as sorption/desorption) that may influence its mobility and distribution.

Given the redox conditions on the surface of the Earth, the predominant and stable form of phosphorus over all typical environmental pH values should be the pentavalent (+V) species (see Eh/pH diagram in Figure 3.11). This figure is a graphical representation of equilibria between chemical species as both a function of pH and redox potential or electron activity (Eh or pe). Equations used to generate Figure 3.11 can be found in Table 3.2. Electron activity is given by

\[ p_e = -\log a(e^-). \]  

In determining pe, one must find the standard reduction potential \( E^0 \) for the half-reaction of interest. A large negative value of pe indicates a condition that favors reduction. A large positive pe indicates a condition that favors oxidation. The electrode potential, Eh, is related to pe by the equation

\[ pe = \frac{F}{2.30RT}Eh, \]
where $F =$ Faraday’s constant (96.42 kJ volt$^{-1}$ eq$^{-1}$), $R =$ gas law constant (8.314 J/(k mol)), and $T =$ temperature (K). At 25°C, this becomes

$$\text{pe} = 16.9 \text{Eh}, \text{ or Eh = 0.059 pe.}$$

Note that the Eh and pH of an aqueous solution are related. For a given half-cell equation

$$aA + bB + ne - + hH^+ = cC + dD.$$  

The half-cell standard potential $E^\circ$ is given by

$$E^\circ(V) = -\frac{\Delta G}{nF}, \quad (3.28)$$

where $\Delta G$ is the Gibbs free energy change, $n$ is the number of electrons involved, and $F$ is Faraday’s constant. The Nernst equation then relates pH and Eh:

$$\text{Eh} = E^\circ + \frac{0.0592}{n} \times \log \left\{ \frac{[A]^a[B]^b}{[C]^c[D]^d} \right\} - \left( \frac{0.0592h}{n} \right) \text{pH}. \quad (3.29)$$

FIGURE 3.11 Eh/pe–pH diagram for phosphorus species in water. For calculations involving equilibrium between reduced phosphorus species and phosphine (i.e., dashed lines including PH$_3$), an equilibrium concentration of $10^{-6}$ M for the reduced phosphorus compound was assumed. The dashed line with P$_{H_2}=1$ atm is shown as a reference for a reducing environment on Earth.
In spite of the importance of the Eh its experimental measurement in a natural environment is still not entirely resolved. However, if correct thermodynamic data are available, it is possible to propose viable models to determine conditions of natural redox systems. Nonetheless, natural waters range between pH values of 4 and 10 and between Eh values of $+1000$ and $-600$ mV, suggesting that based on equilibrium considerations, reduced phosphorus should not be present in natural waters. However, despite the low Eh environments in which reduced phosphorus species are expected to exist, phosphorus in the $\text{III}$ oxidation state has been detected in the environment and has been shown to be relatively stable in the presence of oxygen and absence of other catalysts. If we, however, extend our definition of “natural waters” to include unusual and acidic aquatic environments such as those associated with acid mine drainage, the lower limit of Eh values in acidic environments (pH = 1 or lower) can be below $-800$ mV. In such environments, the fully protonated form of phosphite, $\text{H}_3\text{PO}_3$, is thermodynamically stable.

**TABLE 3.2 Half-Reactions and Thermodynamic Constants Involving Phosphate, Phosphite, and Hypophosphite Species**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$E^\circ$ (V)*</th>
<th>$p\text{e}^\circ$*</th>
<th>log $K$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_3\text{PO}_4 + 2e^- + 2H^+ \rightarrow \text{H}_3\text{PO}_3 + H_2O$</td>
<td>$-0.69$</td>
<td>$-11.695$</td>
<td>$-23.390$</td>
</tr>
<tr>
<td>$\text{H}_3\text{PO}_4 + 2e^- + H^+ \rightarrow \text{H}_2\text{PO}_3 + H_2O$</td>
<td>$-24.690$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{H}_2\text{PO}_4^- + 2e^- + 2H^+ \rightarrow \text{H}_2\text{PO}_3^- + H_2O$</td>
<td>$-22.590$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{H}_2\text{PO}_4^- + 2e^- + H^+ \rightarrow \text{HPO}_2^2^- + H_2O$</td>
<td>$-29.290$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{HPO}_2^- + 2e^- + 2H^+ \rightarrow \text{HPO}_2^- + H_2O$</td>
<td>$-22.090$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{PO}_3^- + 2e^- + 3H^+ \rightarrow \text{HPO}_2^- + H_2O$</td>
<td>$-9.390$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{H}_3\text{PO}_3 + 2e^- + 2H^+ \rightarrow \text{H}_3\text{PO}_2 + H_2O$</td>
<td>$-0.913$</td>
<td>$-15.475$</td>
<td>$-30.95$</td>
</tr>
<tr>
<td>$\text{H}_3\text{PO}_3 + 2e^- + H^+ \rightarrow \text{H}_2\text{PO}_2 + H_2O$</td>
<td>$-32.05$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{H}_2\text{PO}_3^- + 2e^- + 2H^+ \rightarrow \text{H}_2\text{PO}_2^- + H_2O$</td>
<td>$-30.75$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{HPO}_2^- + 2e^- + 3H^+ \rightarrow \text{H}_2\text{PO}_2^- + H_2O$</td>
<td>$-24.05$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{H}_3\text{PO}_2 + e^- + H^+ \rightarrow \text{P}^+ + 2H_2O$</td>
<td>$-0.922$</td>
<td>$-15.627$</td>
<td>$-15.627$</td>
</tr>
<tr>
<td>$\text{H}_2\text{PO}_2^- + e^- + 2H^+ \rightarrow \text{P}^+ + 2H_2O$</td>
<td>$-14.527$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{P}^+ + 3e^- + 3H^+ \rightarrow \text{PH}_3(\text{g})$</td>
<td>$-0.525$</td>
<td>$-8.898$</td>
<td>$-26.7$</td>
</tr>
<tr>
<td>$\text{H}_3\text{PO}_2 + 4e^- + 4H^+ \rightarrow \text{PH}_3(\text{g}) + 2H_2O$</td>
<td>$-42.322$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{H}_3\text{PO}_3 + 6e^- + 6H^+ \rightarrow \text{PH}_3(\text{g}) + 3H_2O$</td>
<td>$-73.271$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*p$ $\text{e}^\circ = p\text{e}$ in standard state.
These observations suggest that the kinetics of chemical oxidation of these species may be relatively slow with respect to the equilibrium conditions depicted in Figure 3.11. Thus, given potentially slow redox kinetics, it would be expected that reduced forms of phosphorus may exist in highly reducing microcosms in nature but that, thus far, have circumvented detection due to limitations in detection capabilities. Moreover, microorganisms (rather than chemical oxidants) are likely to be the catalysts or mediators of redox-reactions that rapidly cycle reduced phosphorus to phosphate in the environment. The strongest evidence for the existence of a detectable redox cycle for phosphorus is in the microbiology literature. The idea of the biological formation of reduced gaseous phosphorus compounds dates back more than 100 years.

3.3.4. Trace Metals in Natural Waters

The study of metals in aquatic ecosystems is an extremely important and complex environmental issue. The complexity stems partially from the fact that trace metals in natural waters are present in a variety of forms having different reactivities and bioavailabilities. The determination of oxidation states is an important consideration for metal toxicity, especially for elements such as arsenic (As), selenium (Se), and chromium (Cr). Let’s consider the former in greater detail. In natural waters, As exists in a variety of forms including the inorganic species arsenite [As(III)] and arsenate [As(V)] as well as those bound to particulates and organic matter. As(III) and As(V) species are considered the most abundant species, with As(V) being thermodynamically stable under oxic conditions. In reducing conditions, such as those in naturally occurring geothermal systems, As(III) dominates (Wilkie and Hering, 1998). As(III) is more toxic than As(V), with both affecting the health of millions of people worldwide. Ultimately, the concentrations and speciation of As(III) and As(V) are determined by various abiotic and biologically mediated biogeochemical processes. (See Research Application II for a greater discussion on redox-sensitive As species.)

**TEXTBOX 3.4**

Oxic waters are defined as having chemically active dissolved oxygen levels. In contrast, anoxic waters are areas that are depleted of dissolved oxygen. Typically, such conditions occur if the rate of oxidation of organic matter by bacteria is greater than the supply of dissolved oxygen.

Organometallic species (covalently bonded molecules) are also of great importance when studying aquatic ecosystems. For example, methylmercury (CH$_3$Hg$^+$) is of immense environmental importance because its toxicity is even greater than Hg$^{2+}$. Such a high level of toxicity stems from the fact that it is highly membrane permeable and has a strong tendency to bind to tissues. In
acidiﬁed aqueous solutions, the mechanism of the electrochemical reduction of \( \text{CH}_3\text{Hg}^+ \) proceeds as follows:

\[
\begin{align*}
\text{CH}_3\text{Hg}^+ + e^- &= \text{CH}_3\text{Hg}^* \\
2\text{CH}_3\text{Hg}^* &\rightarrow (\text{CH}_3\text{Hg})_2 \\
(\text{CH}_3\text{Hg})_2 &\rightarrow (\text{CH}_3)_2\text{Hg}^+ + \text{Hg}
\end{align*}
\]

The above mechanism suggests that the reduced methylmercury radicals can quickly undergo a fast dimerization reaction, with the reactions eventually leading to the formation of dimethyldimercury. As shown from the example above, organometallic species can be produced naturally from inorganic precursors, i.e., by chemical or biological methylation. Note that they are also formed via industrial processes and introduced into the environment as biocides in agriculture, fuel additives, or antifouling paints. Ultimately, the bioavailability and toxicity of metals are influenced by the physico-chemical characteristics of the forms in which they are present (termed speciation) and the physiological characteristics of a given organism. Note that biological availability of a trace metal is not a function of total metal concentration, but rather of particular species of the metal that either can interact directly with an organism or can readily convert to species that can interact (the kinetically labile metal concentration). The interactions between chemical species in the environment and aquatic organisms are complex, and their elucidation requires interdisciplinary approaches and detailed knowledge of relevant chemical, physical, and biological processes. Such processes will be given full consideration throughout this book.

Research Application II: Redox Conditions and Arsenic Speciation and Transport

To extend our discussion of redox-sensitive environmental species consider the following research application highlighting the study of arsenic mobility in groundwater in China (Xie, et al., 2009). In addition to selected regions of China, high arsenic groundwater concentrations have been documented in Argentina, Bangladesh, Chile, India, Mexico, and the United States. Such occurrences are significant and timely given the current state of global drinking water supplies and lack of treatment facilities, especially in regards to developing nations. The selected application focused on the importance and control of arsenic mobilization along three flow pathways in the northern Datong Basin—an area of China home to numerous rural villages and high population densities. Concentrations ranged from 68 to 670 \( \mu \text{g} \text{ L}^{-1} \) in the central basin and 3.1 to 44 \( \mu \text{g} \text{ L}^{-1} \) in the western and eastern regions. In the latter, highly oxidized waters were evident with low contents of As(III) and high proportions of As(V). In contrast, the central basin contained highly reducing waters with high proportions of As(III) among As species.

In order to mitigate the health hazards that arsenic may pose in these and other communities, we must better understand the processes that lead to the
mobilization of arsenic within groundwater systems. The authors discuss a number of mechanisms that likely control arsenic mobilization, including arsenic being sorbed and sequestered on Fe/Mn oxides, reductive dissolution of Fe(III) hydroxides, and sulfide oxidation. While the latter may be a source of arsenic, microbial sulfate reduction could result in the reduction of arsenic concentrations in groundwater through the formation of pyrite, which could precipitate/sorb arsenic. As a result, sulfur isotope values of dissolved sulfate may indicate sulfate reduction and that in turn may provide insights into reaction pathways and conditions that mobilize or retard arsenic. Ultimately, the authors used an integrated approach to studying arsenic distribution and mobilization involving the following processes and factors: Eh measurements, Fe-hydroxide sorption studies, sulfur cycle link considerations, and study of the behavior of other redox-sensitive species (Mo, U, and nitrate). Their study area included 15 groundwater wells and two springs located in the central and outer regions of the Datong Basin.

In terms of results, the authors noted that the mobility of sulfate, U, and Mo was controlled by the change in redox conditions as the groundwater flowed toward the central basin. Reducing conditions along the pathway could not account for the occurrence of high arsenic concentrations but did provide insight into arsenic speciation. As expected, all groundwater wells with As(III) as the major As species showed low Eh values. In contrast, those with As(V) demonstrated high Eh values. Reductive dissolution of Fe-oxyhydroxides or reduction of As(V) were consistent with these observations. In terms of sulfur isotope data, no significant correlations were observed between sulfur isotope values and total arsenic concentrations. The authors stressed that limited evidence for sulfate reduction was observed, thus indicating that sulfate reduction did not sequester arsenic. Overall, the data were consistent with traditional models of arsenic mobilization (see Figure 3.13): those that considered reductive dissolution of Fe-oxyhydroxides, reduction of As(V) to more mobile As(III), and bacteria-mediated reactions (due to the presence of organo-arsenic compounds) as active processes. This application provided further information in regards to the study of arsenic mobilization in groundwater processes. Students and faculty are encouraged to explore this paper and other relevant papers for a greater appreciation of this topic and its importance in global drinking water considerations.

3.4. DISSOLUTION AND PRECIPITATION IN AQUATIC ENVIRONMENTS

A good understanding of the processes of dissolution and precipitation is essential for a quantitative assessment of contaminant fate and transport in aquatic environments. Unlike our previous discussions of dissolved species, dissolution and precipitation reactions are typically slower, although rates are difficult to generalize. For a greater understanding we will first consider equilibrium relations. The equilibrium governing the dissociation of solids in water is given by the general form A(s) ⇌ A(aq), and its equilibrium constant, \( K_{sp} \), is given the name “solubility product.” In the case of ionic compounds, the solubility product equilibrium is usually written in the form
$M_mA_n(s) \rightleftharpoons mM^{n+}(aq) + nA^{m-}(aq)$,
where $M^{n+}$ is the metal cation of charge $n^+$ and $A^{m-}$ is the anion of charge $m^-$. It is important to note the position of the undissociated compound on the left side (i.e., as the reactant) in the $K_{sp}$ equilibrium equation, and the dissociated ions on the right (i.e., as the products). The corresponding general expression for $K_{sp}$ is

$$K_{sp} = \left[M^{n+}\right]^m\left[A^{m-}\right]^n. \tag{3.30}$$

Calculations involving the $K_{sp}$ are usually for the cases of sparingly-soluble or “insoluble” ionic compounds. Values of $K_{sp}$ are typically very small numbers several orders of magnitude smaller than 1. In such cases, one can view the dissociation as being very unfavorable and the concentrations of the dissociated species as being very low in concentration. The process of precipitation (the reverse of dissociation) occurs when ions leave solution to regenerate an ionic solid. The $K_{sp}$ dictates the prediction of formation of precipitates from aqueous solution.

**Example Problem 3.3**

Consider the reaction below:

$$Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2OH^-(aq) \quad K_{sp} = 1.8 \times 10^{-11}.$$ 

Describe the solubility behavior of $Mg(OH)_2(s)$ as the acidity of the solution increases.

**Answer:** As mentioned, the pH of a solution will affect the solubility of any substance whose anion is basic. The solubility of $Mg(OH)_2(s)$ greatly increases as the acidity of the solution increases:

$$Mg(OH)_2(s) + 2H^+(aq) \rightleftharpoons Mg^{2+}(aq) + 2H_2O(l).$$

What factors affect solubility and how does this relate to metal ion behavior in aquatic systems? The common ion effect states the solubility of insoluble substances can be decreased by the presence of a common ion. In addition, we can consider complex ion formation due to the presence of complexing agents. Here, the complexing agent that reacts with the anion or cation of the precipitate increases the solubility of the precipitate. For example, silver chloride, $AgCl$, is reasonably insoluble in water. However, upon the addition of aqueous ammonia, it dissolves appreciably. Consider the equilibria:

$$AgCl(s) \rightleftharpoons Ag^+ + Cl^-$$
$$Ag^+ + NH_3 \rightleftharpoons AgNH_3^+$$
$$AgNH_3^+ + NH_3 \rightleftharpoons [Ag(NH_3)_2]^+. $$
As shown, the ammonia combines with silver ions to form a complex diamminesilver(I) ion. Although this is a reversible reaction, the position of the equilibrium lies well to the right, thus forming a fairly stable complex. In addition, the solubility of a given substance will be affected by the pH of solution if the cation of the substance is a weak acid or the anion is a weak base. For example, metal ions can be considered multi-protic weak acids, where the relative concentrations of the different hydrolysis species are dependent on pH. Upon hydrolysis, the free ions will react with other solutes to form more complex ions. The solubility of hydroxides (and oxides) can be expressed (in general terms) in equilibrium with free ions. Considering divalent metal ions:

\[
\text{Me(OH)}_2(s) \rightleftharpoons \text{Me}^{2+} + 2\text{OH}^-
\]

\[
\text{MeO(s) + H}_2\text{O} \rightleftharpoons \text{Me}^{2+} + 2\text{OH}^-
\]

The conventional solubility product is given by (Stumm and Morgan, 1981)

\[
K_{s0} = [\text{Me}^{2+}] [\text{OH}^-]^2 \text{ mol}^3 \text{ L}^{-1}.
\]

**TEXTBOX 3.5**

**Hydrolysis** is a chemical reaction in which the action of water (or its ions) breaks down a substance into smaller molecules. The most common hydrolysis occurs when a salt of a weak acid or weak base (or both) is dissolved in water.

This constant is corrected for ionic strength and temperature. Note that it is often appropriate to express the solubility in terms of reactions with protons, since the equilibrium concentrations of \(\text{OH}^-\) ions may be exceedingly small. The solubility equation can then be defined as (Stumm and Morgan, 1981)

\[
c K_{s0} = \frac{[\text{Me}^{2+}]}{[\text{H}^+]^2} \text{ mol}^{-1} \text{ L} \quad \text{(3.31)}
\]

And when considering the ion product of water, \(K_w\), we can write

\[
c K_{s0} = \frac{c K_{s0}}{K_w} \quad \text{(3.32)}
\]

The logarithm of the resulting mass action equilibrium for ion concentrations gives a linear equation relating ion concentration and pH. Note that the subscript zero in Equations 3.31–3.32 indicates that the equilibrium of the solid with the uncomplexed species \(\text{Me}^{2+}\) and \(\text{OH}^-\) is considered. Finally, the solubility of metal ions in aqueous solutions is affected by initial metal concentration (impacts the formation of polynuclear complexes), time (affects crystal and polynuclear complex formation), and particle size.
Concerning the behavior of metals in aqueous solutions, if no complexing ligands other than OH\(^-\) are present, the metal cation (M\(^{2+}\)) will tend to hydrolyze to form complexes with OH\(^-\) as a function of pH. Such complexes can be anions, cations, and neutral molecules.

Example Problem 3.4

Hydrogen sulfide H\(_2\)S often occurs naturally in well water, or can be caused by the presence of sulfate-reducing bacteria in a well or water system. It dissolves in water to make a solution that is weakly acidic. Consider a 0.10 M saturated solution of H\(_2\)S and calculate the [H\(^+\)].

Answer: Write the associated equilibria and equilibrium constant expressions:

\[
\begin{align*}
H_2S & \rightleftharpoons H^+ + HS^- \\
HS^- & \rightleftharpoons H^+ + S^{2-} \\
H_2O & \rightleftharpoons H^+ + OH^- \\
K_1 & = \frac{[H^+][HS^-]}{[H_2S]} = 1.0 \times 10^{-7} \\
K_2 & = \frac{[H^+][S^{2-}]}{[HS^-]} = 1.0 \times 10^{-14} \\
K_w & = [H^+][OH^-] = 1.0 \times 10^{-14}.
\end{align*}
\]

Next, we write the charge balance equation: [H\(^+\)] = [HS\(^-\)] + [OH\(^-\)] + 2[S\(^{2-}\)].

And the mass balance equation: C = [H\(_2\)S] + [HS\(^-\)] + [S\(^{2-}\)]. From this system we can make the assumption that [OH\(^-\)] is negligible, and since \(K_2 < K_1\), we can neglect the second dissociation step above. Here, [S\(^{2-}\)] is considered negligible and [H\(^+\)] is roughly equal to [HS\(^-\)]. Next, we can simplify our mass balance and charge balance equations from above:

\[
C = [H_2S] + [HS^-] \\
[H^+] = [HS^-].
\]

If we combine our first dissociation step with the simplified charge and mass balance equations above, the following relationship results:

\[
K_1 = 1.0 \times 10^{-7} = \frac{[H^+]}{C - [H^+]}.
\]

We can then solve for [H\(^+\)]:

\[
[H^+] = \sqrt{1.0 \times 10^{-7} \times 0.10} = 1.0 \times 10^{-4}.
\]

3.5. ADSORPTION IN AQUATIC ENVIRONMENTS

As discussed, the behavior of many elements present in macroconcentrations in aquatic systems is controlled by rules of acid-base equilibria, solubility, and
complexation with the extent of elements participating in such reactions determined by the kinetics (rates) and thermodynamics of involved reactions. The behavior of trace elements, however, is largely influenced by the **adsorption** process. Adsorption refers to the process leading to the concentration of a trace element from an aqueous phase onto the surface of a solid phase. Note that this does not apply to coprecipitation and biological uptake activities. In contrast, **desorption** refers to the release into the aqueous phase of previously adsorbed trace elements. **Ion exchange** is considered to be one of the most important adsorption mechanisms for inorganic ions. We will consider this process in greater detail below. The extent of adsorption of inorganic solutes through empirical adsorption equations will be covered in Chapter 8.

Consider our earlier discussion of phosphorus distribution and transformation in section 1.5.4. There has been considerable attention paid to phosphorus adsorption/desorption processes on natural sediments and mineral surfaces. As shown in Figure 1.9, phosphorus will be exchanged on the sediment-water interface until a dynamic equilibrium is reached. Sediments are those mineral and organic materials situated beneath an aqueous layer. Sediment composition varies dramatically and includes such components as metal oxides, iron sulfides, clay minerals, ferric hydroxide, calcite, interstitial microorganisms, and organic matter. Sedimentary organic matter, for example, acts as an important source of nutrients to the overlying water. As discussed in Chapter 1, release of nutrients to the system in sufficient quantities can promote algal blooms, and thus primary productivity is greatly enhanced.

The exchange of phosphorus between water and sediment is driven by both **sorption** reactions and biologically-controlled processes. For example, studies in estuarine environments have shown a two-step ion exchange between clay minerals and water, plus exchange between interstitial microorganisms and water. In lake sediments, the phosphate ion has been shown to be bound by ferric hydroxide (Fe(OH)_3). Here, the processes involving adsorption and subsequent transformation of the phosphate ion become complex. Inorganic phosphate is sorbed by Fe(OH)_3, which is present in the upper oxidized sediment layer. As sediments become saturated with organic matter (devoid of oxygen excess), Fe(III) is reduced. Since Fe(II) salts possess high solubility, Fe^{2+} and inorganic phosphate begin to diffuse. The Fe^{2+} migrates to the boundary of the oxidized zone where Fe(OH)_3 is again precipitated. Inorganic phosphate migrates with Fe^{2+} and eventually becomes bound by the Fe(OH)_3 recently precipitated.

The above processes are complicated by chemical transformations driven by microorganisms. We must also consider ancillary measurements of pH, redox potential, dissolved Ca, Fe, Mn, and alkalinity during our study of the understanding of reactions controlling, for example, phosphorus in solutions in contact with sediments. What role does **seasonal turnover** play in phosphorus exchange? In spring, for example, increasing temperatures,
enhanced sedimentation, and turnover of organic matter occur in shallow lake systems. As a result, the thickness of the oxidized sediment layer decreases and hence the phosphorus binding capacity. What results from this occurrence? The result is release of phosphorus from the surface layer where it was retained during the winter months.

**TEXTBOX 3.7**

**Sorption** is a common term used for both absorption and adsorption. Don’t confuse the latter two terms. Absorption is the incorporation of a substance in one state into another of a different state (e.g., liquids being absorbed by a solid or gases being absorbed by water). Recall that adsorption refers to the process leading to the concentration of a trace element from an aqueous phase onto the surface of a solid phase.

Although phosphorus was used extensively in our discussion, the adsorption of metals from aqueous solutions is of strong interest and environmental significance. Metal ions form soluble complexes with a variety of dissolved ions, including hydroxide, organic acids, carbonate, fluoride, chloride, and sulfate. As a demonstration, consider hydroxide complexes involving zinc (Zn). Refer to the species distribution diagram in Figure 3.12 showing how the solubility of

![Figure 3.12](image_url)  
**Figure 3.12** Species distribution diagram for Zn(OH)₂. This diagram depicts how the solubility of Zn(OH)₂ (s) is determined by the sum of all concentrations of all zinc species across the full pH scale.
Zn(OH)$_2$ (s) is determined by the sum of all concentrations of all zinc species across the full pH scale. Pay particular attention to the dashed lines, which represent the total solubility of Zn(II) species. If we again consider the thermodynamic law of mass action, the solubility for Zn(OH)$_2$ (s) shows that [Zn$^{2+}$] is fixed by pH and the conventional solubility constant (defined above). Figure 3.12 assumes that no complexing ligands other than OH$^-$ are present, and neglects effects that may arise if multiple metals were present in solution. Overall, dissolution and precipitation of metal hydroxides and the carbonate mineral family partially regulate pH and alkalinity of natural waters, ultimately affecting the fate and transport of organic and inorganic contaminants.

The influence of pH on metal adsorption is significant. A primary reason for this is the variability in particle charge, with electrostatic attraction varying depending on the pH value. For example, anions are adsorbed more strongly at

![Figure 3.13](image-url)
a lower pH. Here, the oxides contain many positively charged groups. Cations are more strongly sorbed at higher pH values, likely due to humic substances (see Chapter 8 for a more in-depth discussion) and oxides becoming more negatively charged. We must also consider ionic strength and background electrolytes on the extent of adsorption. Finally, it has also been shown that microalgae display strong adsorption rates for metal ions. The extent of uptake of the different metals with algae is typically assessed under different conditions such as pH, time of algal residence in solution with the metal, and concentration of algal biomass.

3.6. THE BJERRUM PLOT: CONSTRUCTION FROM EXCEL SPREADSHEETS

Recall our discussion of Bjerrum plots in section 3.2.2. As a reminder, Bjerrum plots are graphs that present the distribution of the species as a function of pH, total concentration, and temperature. For the carbonate systems described in Figures 3.7 and 3.8, the species $\text{H}_2\text{CO}_3$, $\text{HCO}_3^-$, and $\text{CO}_2^-$ are of particular interest. Students and instructors are encouraged to read and utilize the informative article by Professor C. Brannon Andersen of Furman University (Anderson, 2002). In it, he describes the use of Excel spreadsheets in constructing and describing theoretical carbonate equilibria. For example, by knowing the total carbon in a given system and using temperature-dependent equations for various equilibrium constants, one can derive a set of equations for the construction of a Bjerrum plot. Entering the equations into a spreadsheet allows the calculation of the log of the species concentration for any given pH. Finally, the plot is constructed by plotting pH versus the log of each of the species concentrations. This article contains valuable content for students learning equilibria concepts (e.g., the concept of carbonate equilibria) and provides an exercise set with supplemental information (e.g., example Excel spreadsheet data) for students and instructors to follow in the course of studying this chapter. Full derivation of the equations presented can be found in cited references within the paper.

3.7. END OF CHAPTER PROBLEMS

3.1 What can water’s polar nature be attributed to? Describe why water is a powerful solvent giving rise to various types of reactions in aqueous solutions.

3.2 Define the term *heat capacity* and discuss its importance in natural water systems.

3.3 How much energy is required to heat 1,000 g of seawater from 18.0°C to 22.5°C?

3.4 How would negative pressure affect the temperature of maximum density of water?
3.5 As discussed, water at 0°C becomes ice and is less dense than its liquid counterpart. As a result, newly formed ice is able to float on the surface of waterbodies, even though it is in a solid state. Describe the significance of this effect in terms of aquatic life.

3.6 Define the term alkalinity. Discuss the main sources of alkalinity in natural water systems.

3.7 Acid mine drainage is acidic water laden with iron, sulfate, and other metals that forms under natural conditions when strata containing pyrite are exposed to the atmosphere or oxidizing environments. Calculate both the \([\text{H}_3\text{O}^+]\) and \([\text{OH}^-]\) of a drainage sample that has a pH of 3.50.

3.8 Using the equilibrium constant expression for the ionization of water, provide an alternative approach to solving the \([\text{OH}^-]\) in problem 3.7.

3.9 Write the charge and mass balance equations for a solution of sodium hydrogen carbonate, \(\text{NaHCO}_3\), noting that it dissociates into \(\text{Na}^+\) and \(\text{HCO}_3^-\). The anion is also known to ionize to \(\text{CO}_3^{2-}\) as well as form carbonic acid, \(\text{H}_2\text{CO}_3\).

3.10 Like \(\text{CO}_3^{2-}\), phosphate (\(\text{PO}_4^{3-}\)) is known to form insoluble precipitates with metal ions in solution. Provide a complete and balanced equation for the reaction of \(\text{Ba}^{2+}\) with \(\text{PO}_4^{3-}\).

3.11 Carbon dioxide dissolved in water is in equilibrium with carbonic acid.
   a) Write the equilibrium expression for this reaction. b) Write two equilibrium expressions for this product in water and discuss the potential consequences of this product formation.

3.12 Would you expect seasonal variations in pCO₂ to exist in seawater? What would be some of the key controlling factors in determining the occurrence and extent of possible variations?

3.13 Describe an open system in terms of pCO₂ and [CO₂] levels.

3.14 Explain ocean chemistry changes that could likely result in significant changes in the global carbon cycle (e.g., increased atmospheric CO₂ levels).

3.15 Discuss why determining dissolved inorganic carbon (DIC) concentrations is vitally important in aquatic systems.

3.16 Discuss potential limitations in determining redox conditions in natural waters.

3.17 During methanogenesis (the formation of methane by microbes), CO₂ is used as an electron acceptor in a reduction half-reaction. Complete and balance this half-reaction:

\[
4\text{H}_2 + \text{CO}_2 \rightarrow - + -.
\]

3.18 Consider the following reaction in a basic solution:

\[
\text{ClO}_2 + \text{OH}^- \rightarrow + \text{ClO}_2^- + \text{ClO}_3^-.
\]

a Show the two half-reactions and label as reduction and oxidation as appropriate.

b Provide the overall balanced reaction.
3.19 What is meant by the term metal “speciation” and why is it important in aqueous systems?

3.20 Name three factors that affect the solubility of a substance in aqueous solutions.

3.21 What role does pH play in metal adsorption?

3.22 Based on your study of Research Application II, and your newfound knowledge of adsorption processes, would you expect greater arsenic adsorption to occur in highly reducing or oxidizing environments? Justify your answer.

3.8 REFERENCES


